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Temperature dependence of the Cl + HN$_3$ reaction from 300 to 480 K

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Abstract

The rate constant for Cl + HN₃ over the temperature range 300–480 K has been studied in a flow reactor. Based on the rate of loss of HN₃ and the rate of NCl(a$^1\Delta$) generation, the temperature dependence of this reaction is described by the collision theory expression $1.2 \pm 0.3 \times 10^{-11} T^{0.5} \exp(-1514 \pm 93/T)$, with $E_0 = 3.0 \pm 0.2$ kcal mol^{-1} or an Arrhenius fit $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$ with $E_a = 2.9 \pm 0.2$ kcal mol^{-1}. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The recent report of a direct measurement of gain [1] on the $I(^2P_{1/2}-^2P_{3/2})$ transition in the NCl(a$^1\Delta$)/I chemical system has increased interest in the use of metastable nitrene halides (NX) as energy donors for iodine-based chemical lasers analogous to the chemical oxygen iodine laser (COIL) [2,3]. There are several important advantages and disadvantages to the use of these molecules, which are isovalent with O₂. The most obvious advantage is generation of the (a$^1\Delta$) states in the gas phase [4–10] rather than the mixed gas/aqueous chemistry that is necessary for COIL operation. On the other hand, the NX(a$^1\Delta$) molecules are much more reactive than O₂(a$^1\Delta$) [11–13], and the scaling issues for generating high concentrations of NCl(a$^1\Delta$) have not yet been resolved. The Cl/HN₃ chemical system

used for the generation of NCl(a$^1\Delta$) is summarized by reactions (1) and (2):

$$Cl + HN_3 \rightarrow HCl + N_3 \tag{1}$$

$$Cl + N_3 \rightarrow NCl(a\,^1\Delta, b\,^1\Sigma^+, X\,^3\Sigma^-) + N_2 \tag{2}$$
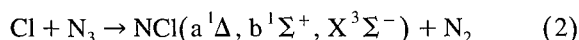
The ΔH_0^0 value for reaction (1) is -9.3 kcal mol^{-1}, and the enthalpy for reaction (2) is -39, -22, and -65 kcal mol^{-1} for generation of the (a$^1\Delta$), (b$^1\Sigma^+$), and (X$^3\Sigma^-$) states, respectively, using ΔH_f^0(NCl) = 77.4 kcal mol^{-1} [14]. The rate determining step for this process is reaction (1), which has a room temperature rate coefficient [15] of $1.1 \pm 0.3 \times 10^{-12}$ cm³ molecule^{-1} s^{-1}. Gain on the $I(^2P_{3/2})-I^*(^2P_{1/2})$ transition was achieved when a small flow of HI is added to a flow of NCl(a$^1\Delta$):

$$Cl + HI \rightarrow HCl + I(^2P_{3/2}) \tag{3}$$

$$NCl(a\,^1\Delta) + I(^2P_{3/2}) \rightarrow NCl(X\,^3\Sigma^-) + I^*(^2P_{1/2}) \tag{4}$$

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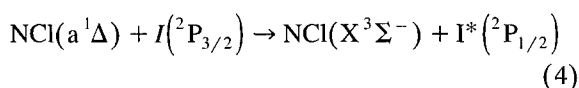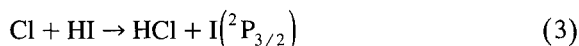
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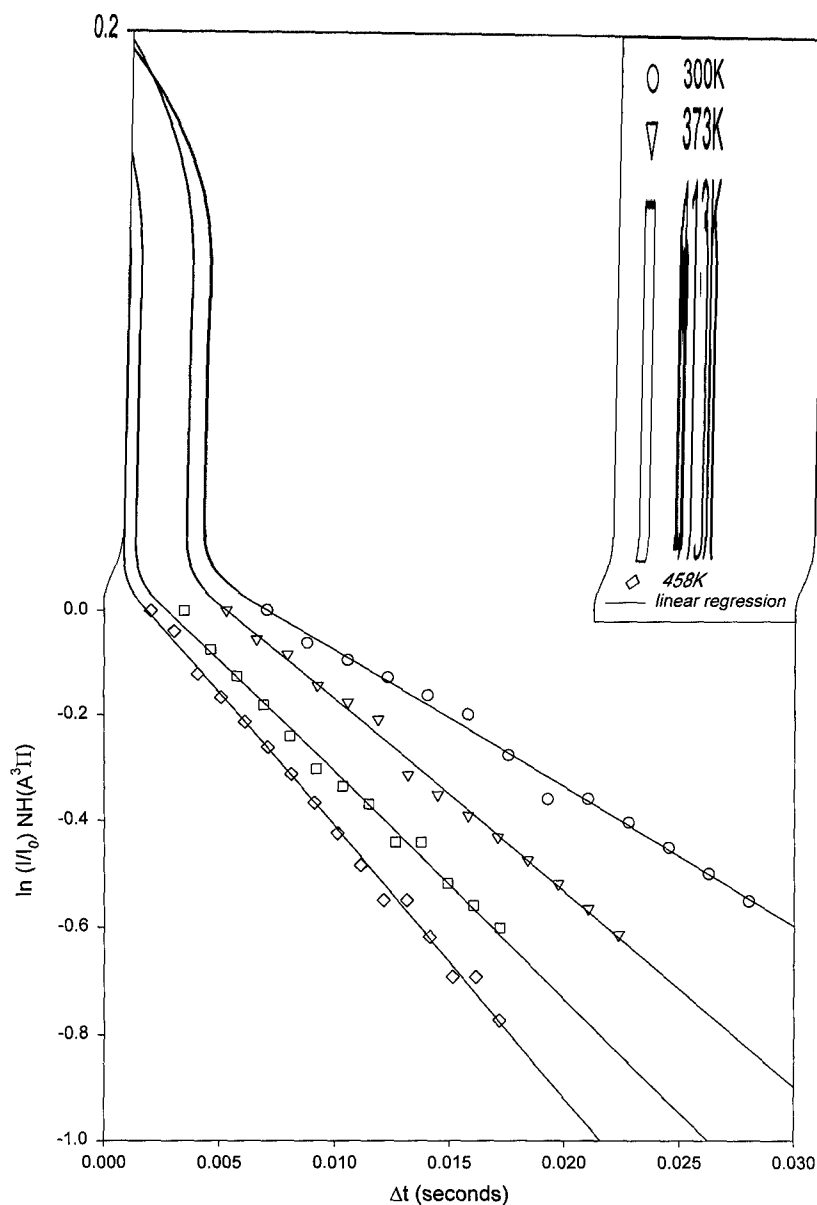
Fig. 2. Pseudo-first-order plots of ln I/I_0(NH(A$^3\Pi$)) versus reaction time. The experimental conditions and results are as follows: (300 K) [Cl] = 1.2×10^{13}, [HN$_3$] = 2.0×10^{12} cm^{-3}, $k = 1.4 \pm 0.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; (373 K) [Cl] = 8.0×10^{12}, [HN$_3$] = 3.0×10^{12} cm^{-3}, $k = 4.5 \pm 0.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; (413 K) [Cl] = 6.0×10^{12}, [HN$_3$] = 2.8×10^{12} cm^{-3}, $k = 6.5 \pm 0.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; (458 K) [Cl] = 6.0×10^{12}, [HN$_3$] = 1.7×10^{12} cm^{-3}, $k = 8.5 \pm 0.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

CF$_3$I in 12 L bulbs. The flow rate of HCl was determined by diverting the stream to a vessel of known volume and measuring the rate of pressure rise. The bulk of the flow (typically 2.5 SLPM, 1850 μm s^{-1}) consisted of Ar (Airgas, UHP grade). Two microwave discharges on a CF$_4$ (Airgas, 99.5%)/Ar mixture produced up to 1.5×10^{13} cm^{-3} F atoms at 1.5 torr. Pre-prepared mixtures of HN$_3$ and He were

stored in a stainless steel vessel. HN$_3$ was added to the reactor via one of two sliding Pyrex injectors.

The entire reactor was encased by resistive heating units, which consisted of Nichrome wire helically wound inside a ceramic jacket. The temperature was measured by inserting several type K thermocouples into the gas stream at various points along the reactor. A flexible thermocouple was inserted

Table 2
Summary of the $k(T)$ measurements via loss of HN$_3$

into the one of the movable injectors to provide a temperature measurement at the center of the tube. The heaters were regulated with Omega controllers (Model CN76000) with an accuracy of $\pm 1°$ at room temperature and $\pm 7°$ at 480 K. All inner surfaces were coated with PTFE, which limited the temperature to 500 K.

A 0.3 m monochromator (Instruments S.A.) dispersed the chemiluminescence collected by a short focal length lens. Two different gratings (500 or 900 nm blaze, both with 1200 grooves mm^{-1}) were used, depending on the emission of interest. The emissions of HF ($\Delta v = -3$), $NF(a\,^1\Delta)$, $NCl(a\,^1\Delta)$, $NF(b\,^1\Sigma^+)$, and $NCl(b\,^1\Sigma^+)$ were monitored with a cooled
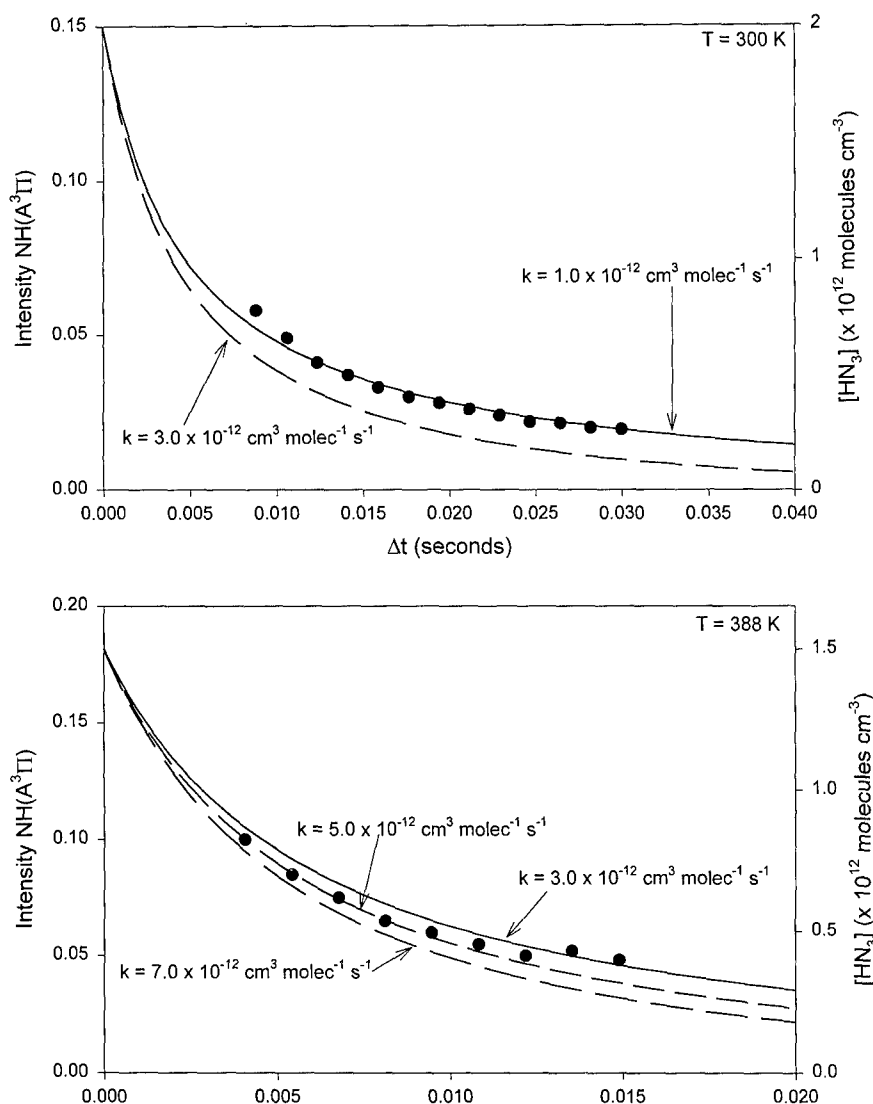
Fig. 3. Non-pseudo-first-order plots of $I(NH(A\,^3\Pi))$ versus reaction time. A least-squares fitting routine was used to extract k_1 from the data. The experimental conditions are as follows. Upper panel: $T = 300$ K, $[Cl] = 1.1 \times 10^{13}$, $[F] = 2.0 \times 10^{12}$, $[HN_3] = 2.0 \times 10^{12}$ cm^{-3}. Lower panel: $T = 388$ K, $[Cl] = 6.5 \times 10^{12}$; $[F] = 1.5 \times 10^{12}$; $[HN_3] = 1.5 \times 10^{12}$ cm^{-3}. Note that the data can be satisfactorily fit by several values for k_1, and the relative error for this method is large.

(−80°C) R1767 PMT (Hamamatsu) while the UV emission from NH(A $^3\Pi$) was detected with a R374 PMT (Hamamatsu) cooled to −50°C. When necessary, band pass or long pass filters were used to isolate signals of interest from unwanted background or second-order emissions. A representative spectrum (uncorrected for the relative response of the S-1

PMT) from the reaction of F and Cl atoms with HN$_3$ is shown in the upper panel of Fig. 1.

The relative concentration of HN$_3$ was monitored by adding N$_2$(A $^3\Sigma_u^+$) via the indicator inlet and monitoring the resultant NH(A $^3\Pi$) signal at 335 nm. The N$_2$(A $^3\Sigma_u^+$) molecules were generated by energy transfer from metastable Ar(^{3}P$_2$, ^{3}P$_0$) atoms using a
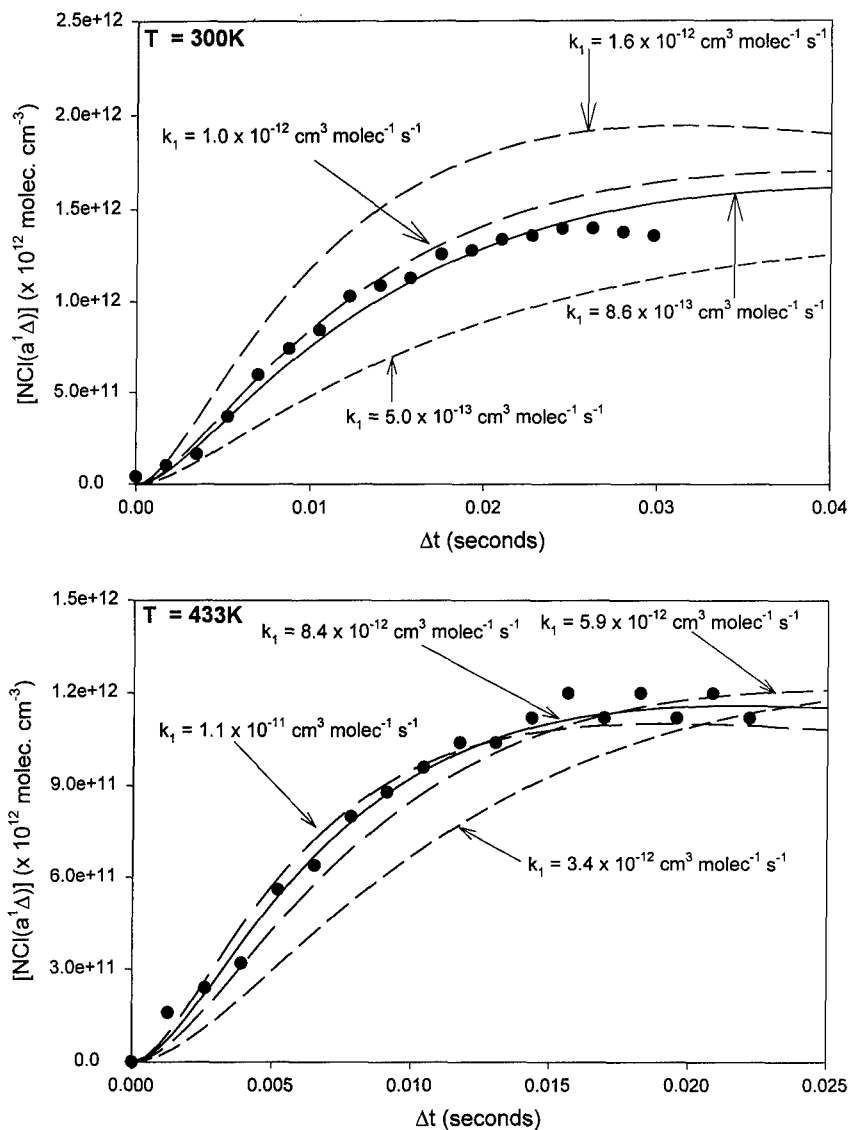
Fig. 4. Measurement of k_1 via generation of NCl(a $^1\Delta$). A least-squares model fit to [NCl(a $^1\Delta$)] versus Δt was used to determine k(Cl + HN$_3$). The experimental conditions are as follows. Upper panel: T = 300 K, [Cl] = 1.8 × 10^{13}, [HN$_3$] = 2.0 × 10^{13} cm^{-3}. Lower panel: T = 433 K, [Cl] = 8.0 × 10^{12}, [HN$_3$] = 1.4 × 10^{13} cm^{-3}. Note that a wide range of values for k_1 can satisfactorily fit the data, and the relative error for this method is large (±30%).

rolled tantalum foil discharge design [21]. The NH($A^3\Pi$) emission intensity increased linearly with the HN$_3$ flow rate (see the lower panel of Fig. 1). With optimization of the light collection and N$_2$($A^3\Sigma_u^+$) generator, [HN$_3$] as low as 1×10^{11} molecule cm^{-3} could be routinely detected even though the branching ratio to (5b) is low.

3. Results and discussion

3.1. Monitoring the loss of [HN$_3$]

Under pseudo-first-order conditions ([Cl] $\gg$ [HN$_3$]) the slope of a given $\ln(I(NH(A^3\Pi)))$ versus Δt plot is equal to k_1[Cl], and the rate constant is given by simply dividing by the known [Cl]. Measurable decomposition of HN$_3$ does not occur below 560 K and reactive loss should be the only removal process [22]. Fig. 2 shows several such measurements taken at a variety of temperatures. In each case, the initial [Cl]$_0$ was determined by first measuring [F]$_0$ and then adding a slight excess of HCl. The intensity decreased with time, and a regression fit to the data gives the product k_1[Cl]. At room temperature, the data is within the combined error bars of the established value for k_1, $1.1 \pm 0.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Several measurements were performed at each temperature and Table 2 lists the average and 2 standard deviations at each temperature. The value of k_1 increases up to $1.1 \pm 0.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for $T = 460$ K.

Because HCl quenches N$_2$($A^3\Sigma_u^+$) ($k_Q = 1.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) [23], it was not always possible to add excess HCl and a few measurements of k_1 were performed with a mix of F and Cl atoms present with HN$_3$. A known flow of HCl is added to a measured [F]$_0$ and [F]' and [Cl]' calculated from the bimolecular rate law. The temporal dependence of [HN$_3$], as monitored by $I(NH(A^3\Pi))$, is fit by the kinetic model listed in Table 1. In cases such as these, accurate measurement of k_1 requires [Cl] $\gg$ [F], and [F] $\leqslant$ [HN$_3$]$_0$. Otherwise, F removes nearly all of the HN$_3$ and it becomes impossible to accurately extract k_1 [5]. Several examples are shown in Fig. 3. In each case, the least-squares analysis produces a satisfactory fit to the data. This method, however, is inherently less sensitive than the method

described above and the error bars for k_1 are significantly larger. Table 2 summarizes the $k(T)$ data for reaction (1) based on the loss of [HN$_3$].

3.2. Generation of NCl($a^1\Delta$)

The rate determining step for the generation of NCl($a^1\Delta$) is reaction (1). For nearly any set of conditions where no [F] is present, the rate of NCl($a^1\Delta$) growth is dependent upon k_1. Fig. 4 shows several examples of the growth of NCl($a^1\Delta$) versus Δt at a variety of temperatures. In each case the linear least-squares fit to the data is indicated by the solid line, while alternate values for k_1 are shown by broken lines. As expected, the established value for k_1 is reproduced at room temperature. However, the precision of this method is quite poor. As the plot shows, several values, up to $\pm 30\%$, also give reasonable fits to the data. This method is also susceptible to error in other ways. For example, as k_1 increases the value of $k_2(T)$ (which was fixed to the room temperature value) becomes more important because N$_3$ and HN$_3$ compete for reaction with [Cl]. Most importantly, it is difficult to generate observable $I(NCl(a^1\Delta))$ without high [Cl]$_0$ and [HN$_3$]$_0$, which may cause additional problems with quenching. Although this method is less satisfactory for the determination of k_1, the results agree quite well with those obtained by monitoring $I(NH(A^3\Pi))$ (see Table 3).

All of the $k(T)$ data for reaction (1) are summarized in Tables 2 and 3 and in Fig. 5. A least-squares

Table 3
Summary of the $k(T)$ measurements via generation of NCl($a^1\Delta$)

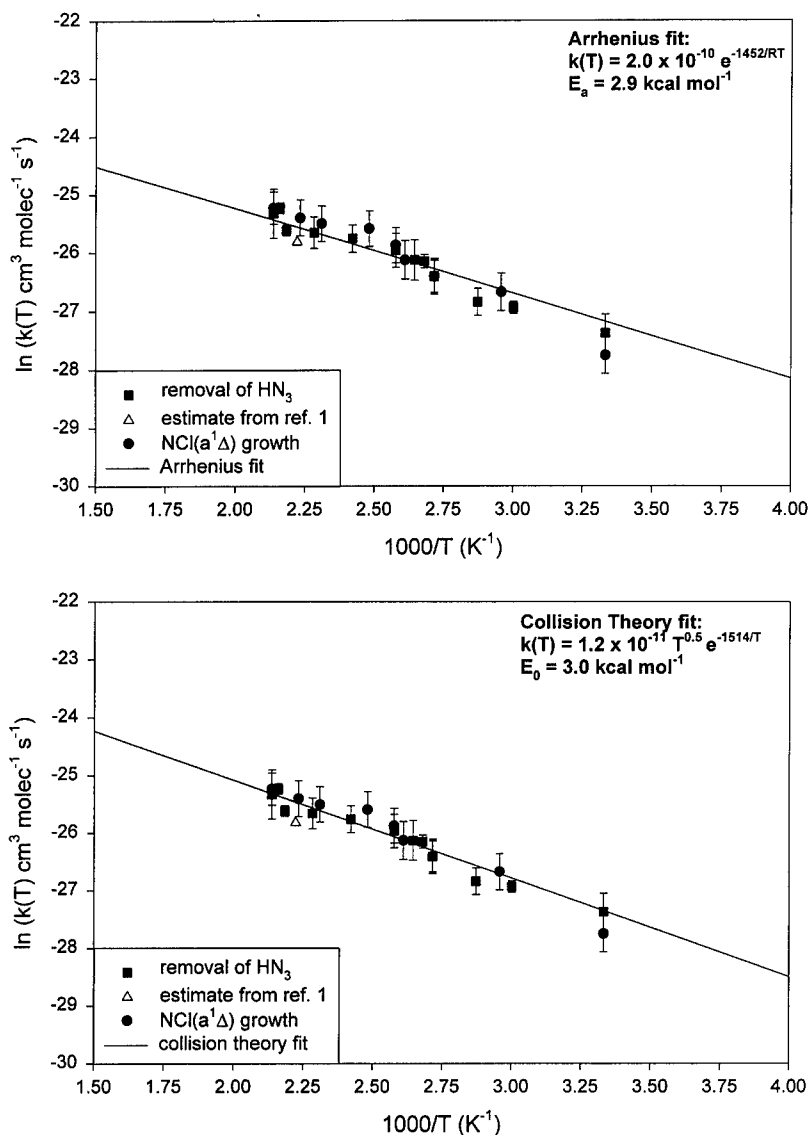| T (K)	$k(T)$ ($\times 10^{-12}$ cm^3 molecule^{-1} s^{-1})
300	0.89 ± 0.27
338	2.6 ± 0.8
368	3.4 ± 1.0
383	4.8 ± 1.4
388	5.8 ± 1.7
403	7.7 ± 2.3
433	8.4 ± 2.5
448	9.3 ± 2.8
468	11 ± 3

Fig. 5. Arrhenius and collision theory fits to the $k_1(T)$ data. Upper panel: The $k_1(T)$ data is fit by the Arrhenius expression. The best fit is achieved for $A = 2.0 \times 10^{-10}$ and $E_a = 2.9$ kcal mol^{-1}. Lower panel: A collision theory expression is used and $A = 1.2 \times 10^{-11}$ and $E_0 = 3.0$ kcal mol^{-1}. In both panels data from both the loss of HN$_3$ and generation of NCl(a $^1\Delta$) techniques are shown.
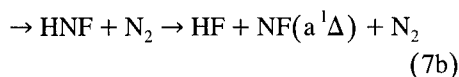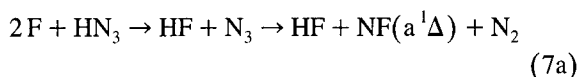
analysis of the data using the collision theory expression, $AT^{0.5} \exp(-E_0/RT)$, results in a satisfactory fit with $A = 1.2 \pm 0.5 \times 10^{-11}$ and $E_0 = 3.0 \pm 0.3$ kcal mol^{-1}. The Arrhenius expression was also used to fit the data: $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$ with $E_a = 2.9 \pm 0.3$ kcal mol^{-1}. The data in Fig. 5 also includes an estimate for k_1 calculated

from the data reported in Ref. [1], and excellent agreement is achieved.

4. Discussion

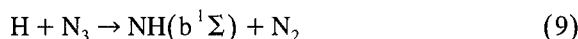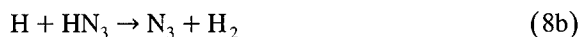While several azide/atom (F, Cl, and H) reactions have been characterized at room temperature,

there have been few measurements for $T > 300$ K. For example, reaction (7)

$$2F + HN_3 \rightarrow HF + N_3 \rightarrow HF + NF(a\,^1\Delta) + N_2 \tag{7a}$$

$$\rightarrow HNF + N_2 \rightarrow HF + NF(a\,^1\Delta) + N_2 \tag{7b}$$

is known to be an efficient source of the N_3 and $NF(a\,^1\Delta)$ radicals. The room temperature rate constant [5] for (7a) is established as $1.1 \pm 0.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and the nascent HF vibrational distribution from reaction (7a) is 0.36:0.36:0.22:0.06 for $v = 1$–4. Microscopic branching between direct abstraction and addition–elimination channels may account for the rather flat vibrational distribution. The branching to HNF (7b) has been established [24] as $0.03^{+0.02}_{-0.001}$. The rate coefficient for the reaction of H atoms with HN_3 has been measured [25] from 300 to 460 K and $k(T) = 2.5 \times 10^{-11} \exp(-2315/T)$ cm^3 molecule^{-1} s^{-1}. The reaction produces $NH_2(^2A_1, \nu_2 \leqslant 20)$ [26] and minor amounts of $NH(A\,^3\Pi)$ and $NH(b\,^1\Sigma)$.

$$H + HN_3 \rightarrow NH_2 + N_2 \tag{8a}$$

The mechanisms for $NH(A\,^3\Pi)$ and $NH(b\,^1\Sigma)$ production are not well established, but they are presumed to be generated by secondary reactions such as [26]:

$$H + HN_3 \rightarrow N_3 + H_2 \tag{8b}$$

$$H + N_3 \rightarrow NH(b\,^1\Sigma) + N_2 \tag{9}$$

$$2NH^*(b\,^1\Sigma \lor a\,^1\Delta) \rightarrow NH(A\,^3\Pi) \tag{10}$$

Prior to this report, the only halogen/azide reaction that had been characterized $T > 300$ K was $Cl + ClN_3$:

$$Cl + ClN_3 \rightarrow N_3 + Cl_2 \tag{11}$$

Combourieu et al. used mass spectrometric detection to measure the temperature-dependent rate constant between 300 and 657 K [27]. They reported a moderate temperature dependence of $k(T) = 2.3 \times 10^{-11} \exp(-554/T)$ cm^3 molecule^{-1} s^{-1}.

The present results indicate a moderate temperature dependence for the reaction of $Cl + HN_3$, with $E_a \approx 3$ kcal mol^{-1}. The pre-exponential factor is large

and requires some comment. Hydrogen atom abstraction reactions such as $F + HCl$ ($k = 4.4 \pm 1.5 \times 0^{-11} \exp(-400 \pm 100/T)$ cm^3 molecule^{-1} s^{-1}) 28] and $Cl + HBr$ ($k = 4.8 \times 10^{-11} \exp(-454/T)$ cm^3 molecule^{-1} s^{-1}) [29] have A factors which are ~ 2–3 smaller than the present result. Halogen atom addition reactions, on the other hand, typically have much larger pre-exponential factors. For example, a relevant comparison may be made with the fast reaction $F + HN_3$, $A \geqslant k_{300} = 1.1 \pm 0.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Chlorine atoms are known to add to olefins (e.g., C_2H_4 [30], C_2H_3Br [31], and C_2H_3Cl [32]) and these reactions are very fast at room temperature, $k(300) = 1.5 \pm 0.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The Cl + olefin reactions also have very small activation energies, probably on the order of a few hundred cal mol^{-1}. For example, assuming $E_a = 0.3$ kcal mol^{-1}, and using $k_{298}(Cl + C_2H_3Br) = 1.43 \pm 0.29 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, the A factor is 2.4×10^{-10} cm^3 molecule^{-1} s^{-1}. Clearly, the large pre-exponential factor for $Cl + HN_3$ is consistent (i.e., within a factor of 2–3) with other Cl atom reactions and is suggestive of a Cl atom addition reaction rather than hydrogen abstraction.

The main products for reaction (1) are assumed to be HCl and N_3 even though vibrationally excited HCl has not been observed (only $HCl(v = 1)$ is energetically possible) and the generation of HNCl cannot be ruled out. Independent confirmation of this could be accomplished in one of several ways: laser-induced fluorescence detection of N_3 or infrared absorption of $HCl(v = 0, 1)$ generated by reaction (1) are the most easily implemented. Virtually nothing is known about the species HNCl. If one assumes that $Cl + HNCl$ is sufficiently exothermic to give $NCl(a\,^1\Delta)$, by analogy to the $F + HN_3$ system, both N_3 and HNCl should react rapidly with Cl atoms to give $NCl(a\,^1\Delta)$.

5. Conclusions

The temperature dependence of the reaction $Cl + HN_3$ has been measured in a heated flow reactor. The rate coefficient was measured by monitoring the loss of HN_3 and the rate of generation of $NCl(a\,^1\Delta)$ versus time for known starting concentrations. The

rate constant data was fit by an Arrhenius expression of $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$ with $E_a = 2.9 \pm 0.3$ kcal mol^{-1}. A collision theory fit to the data gave the expression $1.2 \pm 0.5 \times 10^{-11} T^{0.5} \exp(-1514 \pm 150/T)$, with $E_0 = 3.0 \pm 0.3$ kcal mol^{-1}.

Acknowledgements

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